Optimization of Ion Transport in High Energy Composite Electrodes

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University of California, San Diego
June 2016

Project ID ES216

Overview

Timeline

- April 1st, 2013
- March 31st, 2017
- Percent complete: 75%

Barriers

- Barriers addressed
  - Low rate
  - Poor voltage stability
  - First cycle inefficiency

Budget

- Total project funding
  - US$ 899,999
- Funding received in FY16- US$ 225,000
- Funding for FY16
  - US$ 225,000

Partners

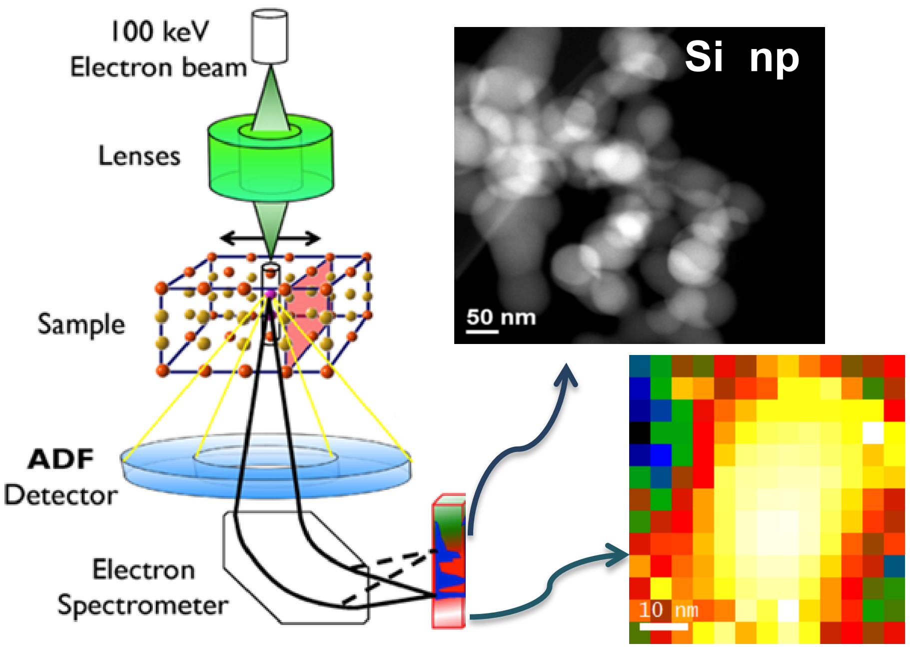
- Interactions/ collaborations
  - Envia Systems
  - Oak Ridge National Lab
  - University of Texas at Austin
  - National Renewable Energy Laboratory
  - Ningbo Institute of Materials Technology & Engineering

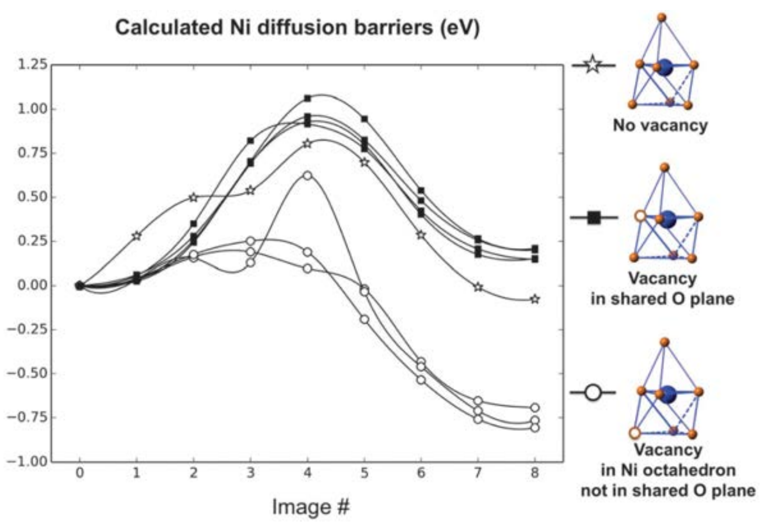
Relevance and Project Objectives

- ❑ Probe and control the atomic-level kinetic processes that govern the performance limitations in terms of rate capability and voltage stability in high energy composite electrodes

- ❑ Use suite of powerful analytical tools diagnose optimum bulk compositions and surface characteristics to improve the mechanistic rate and cycling performance

- ❑ Extend STEM/EELS and XPS techniques to silicon anode types





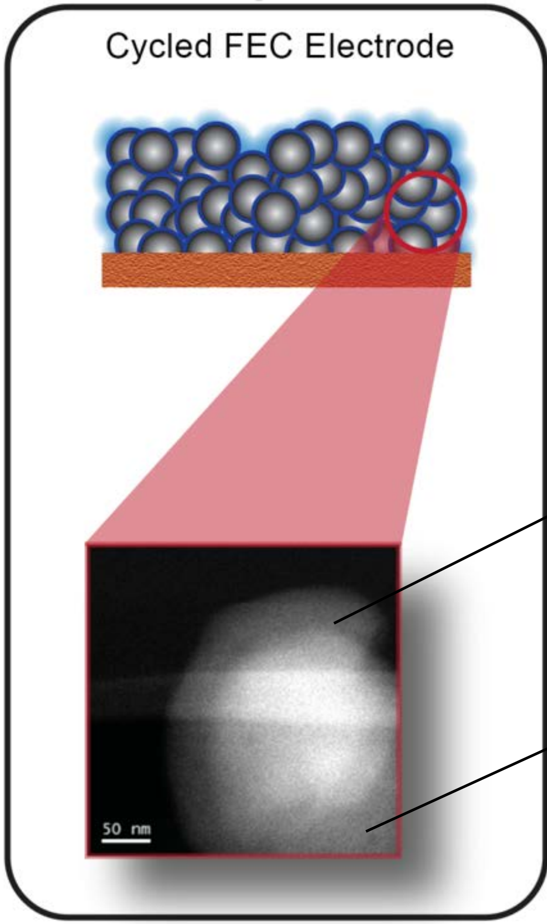
Milestones

- Identify the path-specific lithium dynamics in lithium rich layered oxides. (Compare high Li-rich (HLR), $Li_{1.193}$ material, and low Li-rich (LLR), $Li_{1.079}$ material. (12/30/15) **Complete**
- Investigate the mechanism of improved performance in high voltage Li rich Mn rich layered oxides with LLTO coating (03/31/16) **Complete**
- Quantify the SEI characteristics of ALD and MLD coated silicon anode upon long cycling with combination of STEM/EELS and XPS (06/30/16) **Complete**
- Go/No-Go Milestone: Complete the efforts on investigation of surface modification and morphology control for Li rich Mn rich layered oxides. Criteria: Discontinue studies if the voltage retention does not get improved by 50% in 100 cycles. (06/30/16) **On Track**
- Identify the optimum surface modification and morphology control of silicon/carbon anode with >87% first cycle capacity retention and > 99% columbic efficiency (09/30/16) **On Track**

Approaches/Strategies

Combine atomistic modeling, scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), Neutron Diffraction (ND) to provide an in-depth understanding of surface modifications and bulk substitution to further improve ion transport in high voltage composite materials

Silicon composite electrode



Neutron Diffraction

Oxygen Vacancy

EELS/XAS

Transition Metal oxidation change (Ni,Mn)

EELS/XPS

Li_xSi_y alloys

SEI composition

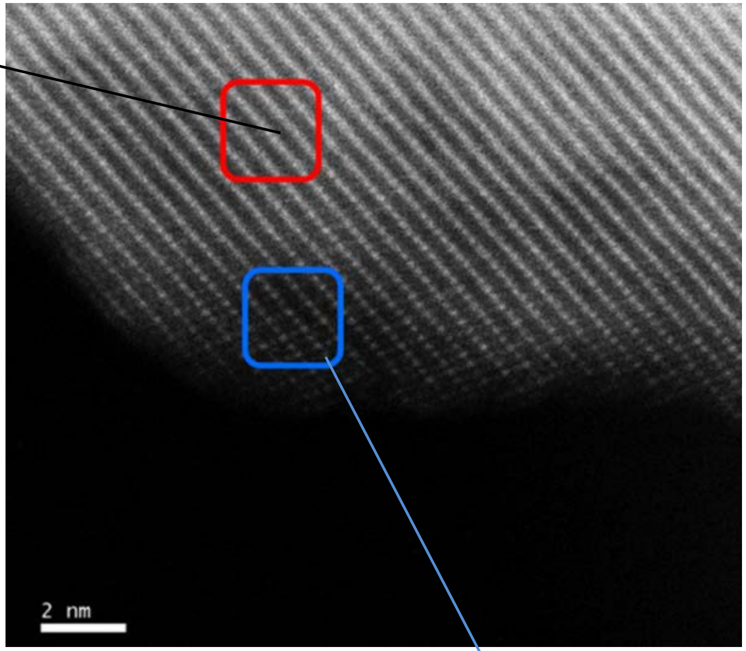
Observe inorganic species

STEM

Volume Expansion

Direct particle visualization

SEI morphology



XPS

Mn oxidation change

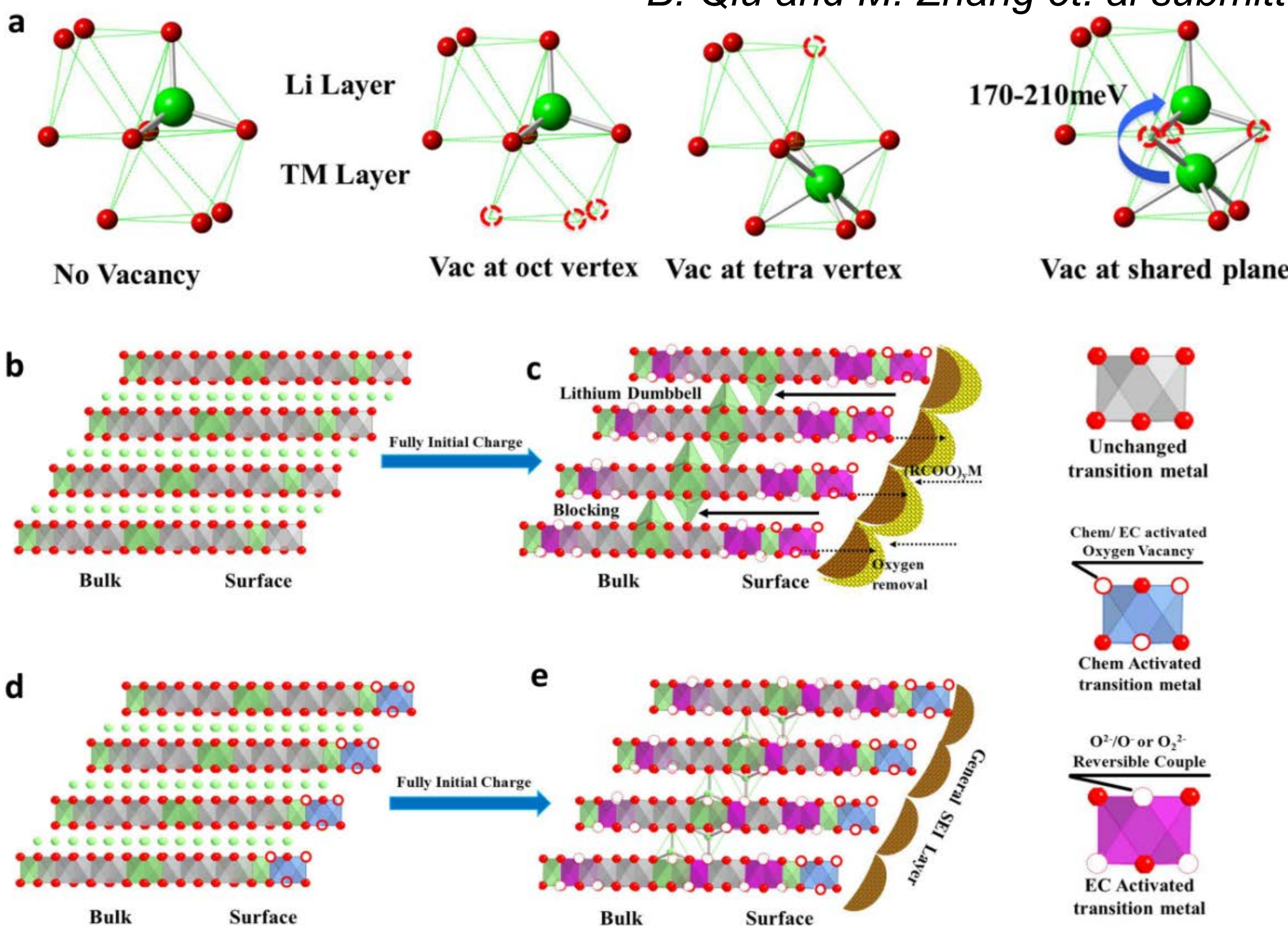
Inorganic SEI compounds

Accomplishment to Date FY 16

Role of Oxygen Vacancy

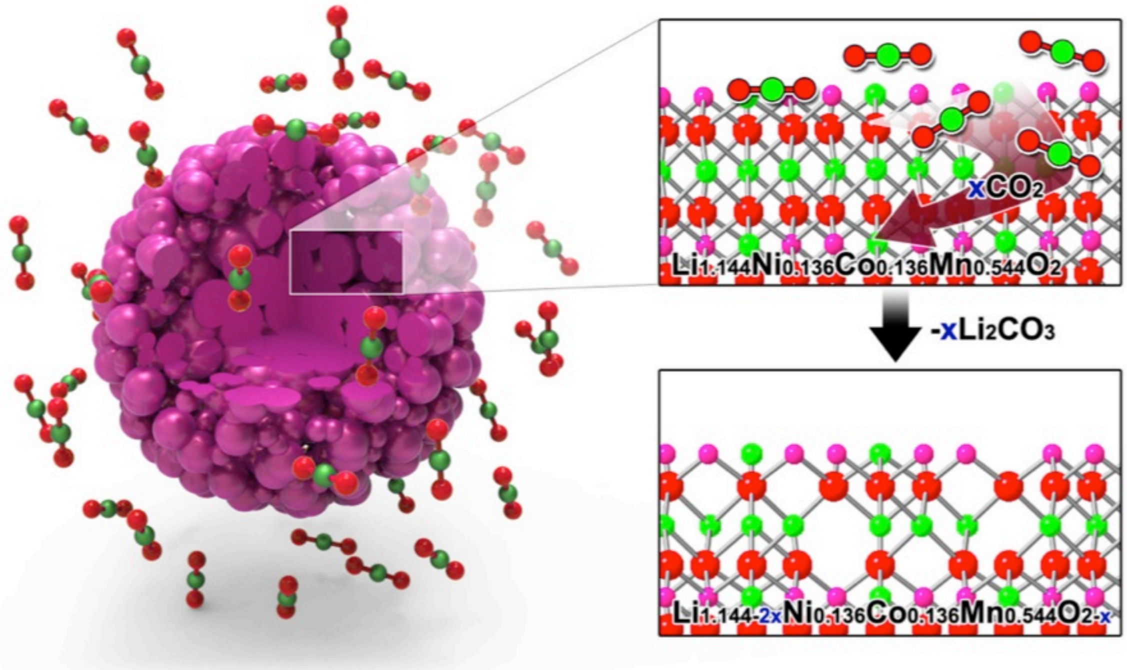
In the presence of O vacancy, tetrahedral Li becomes mobile

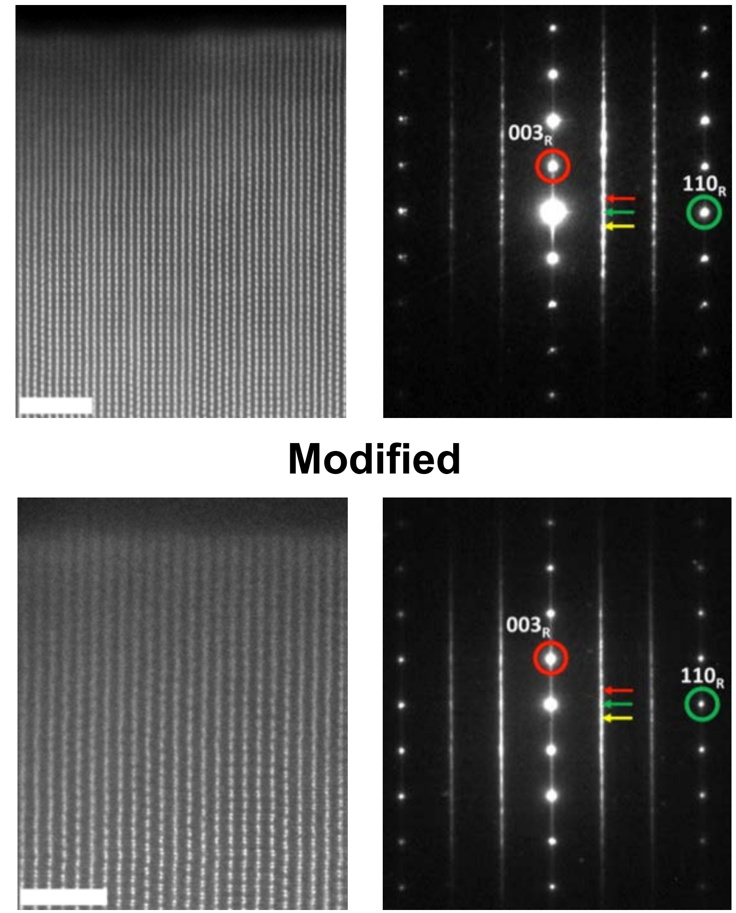
B. Qiu and M. Zhang et. al submitted, 2016



Accomplishments to Date FY16

Manipulate Surface Oxygen Vacancy





Modified

HADDF-STEM **ED**

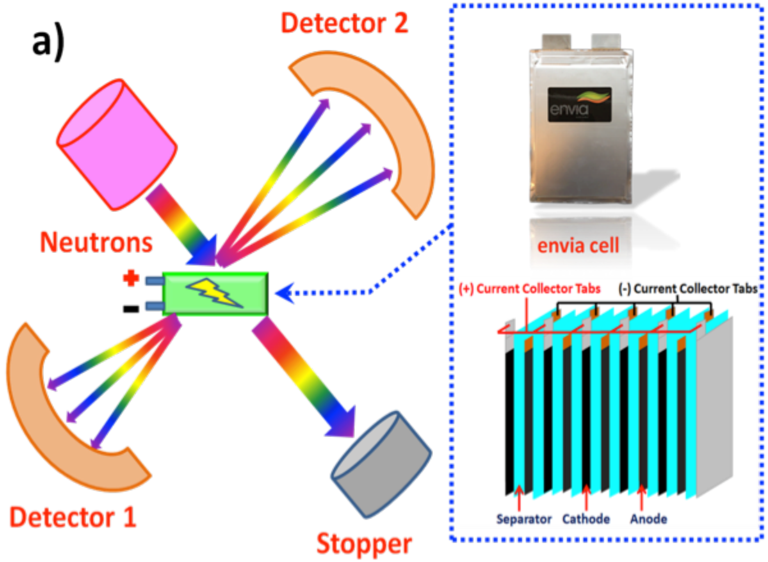
5nm

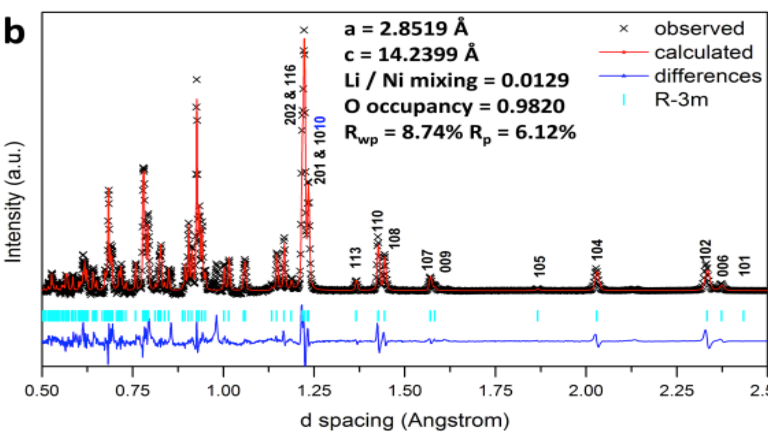
No phase transitions has been observed after creation of oxygen vacancy at surface of Li-rich.

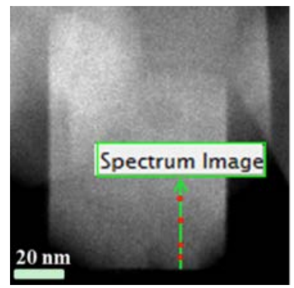
Collaboration with Prof. Liu from NIMTE

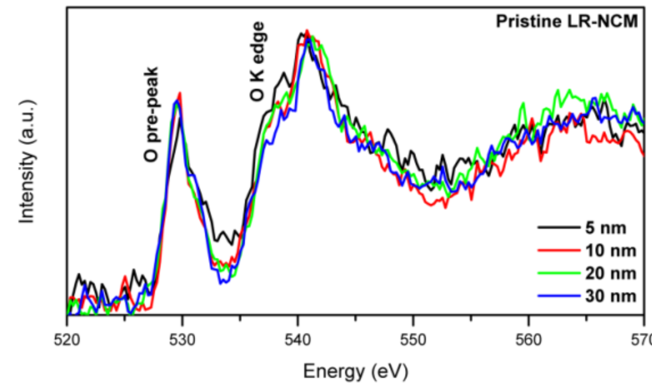
B. Qiu and M. Zhang et. al submitted, 2016

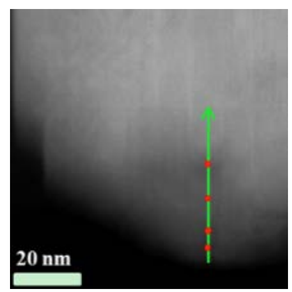
Accomplishments to Date FY16
Quantifying Oxygen Vacancies

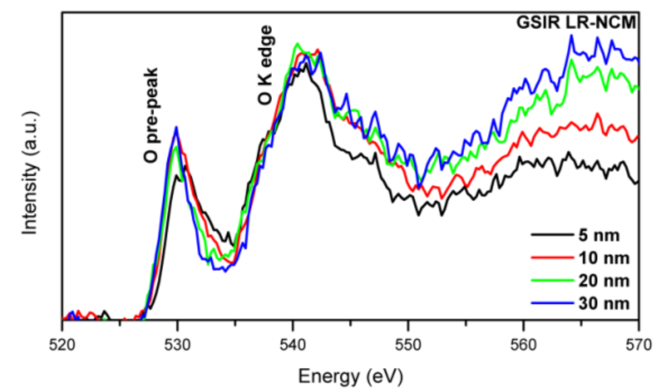












H. Liu and S. Hy et. al Advanced Energy 2016, 1502143

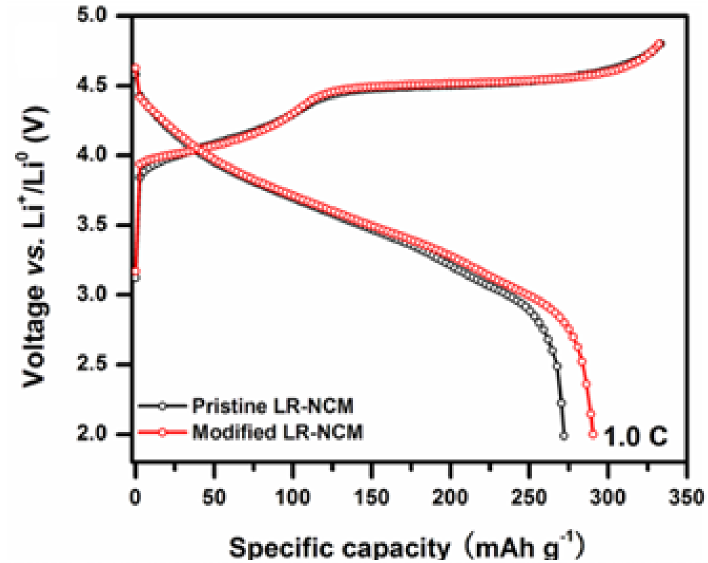
B. Qiu and M. Zhang *et. al* submitted, 2016

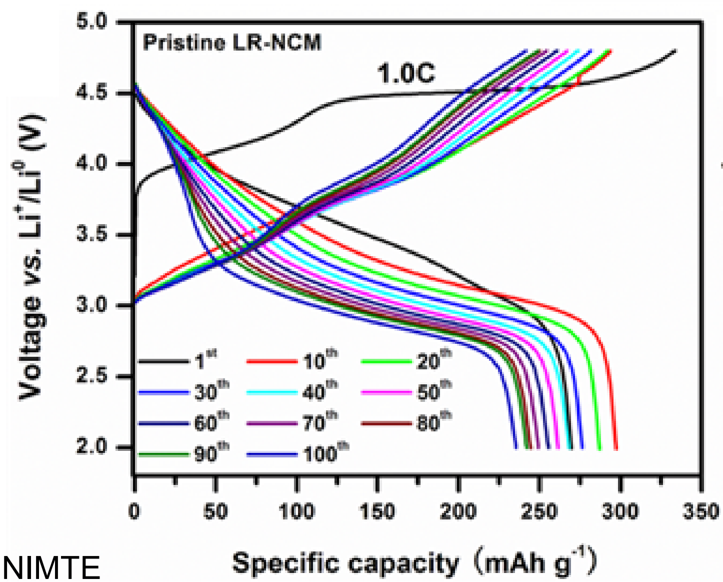
Combining ND and STEM/EELS results show oxygen vacancies form on the sub 2-10nm surface

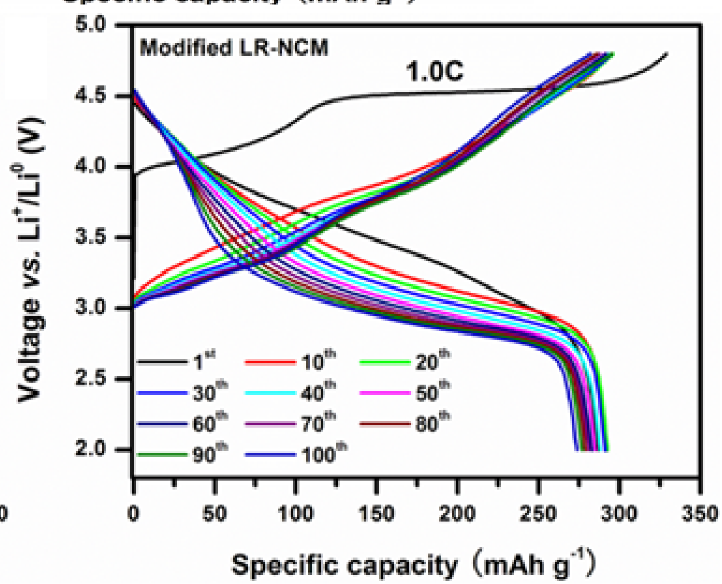
Accomplishments to Date FY16 Comparison of Electrochemical Performance at High Temperature

Elevated Temperature 55°C

Surface modified material shows better capacity retention and less voltage degradation at high temperature



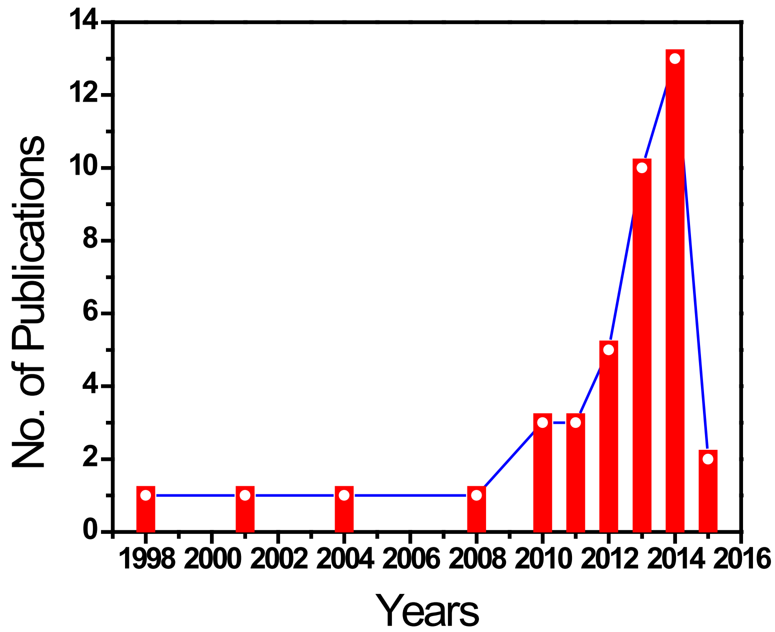




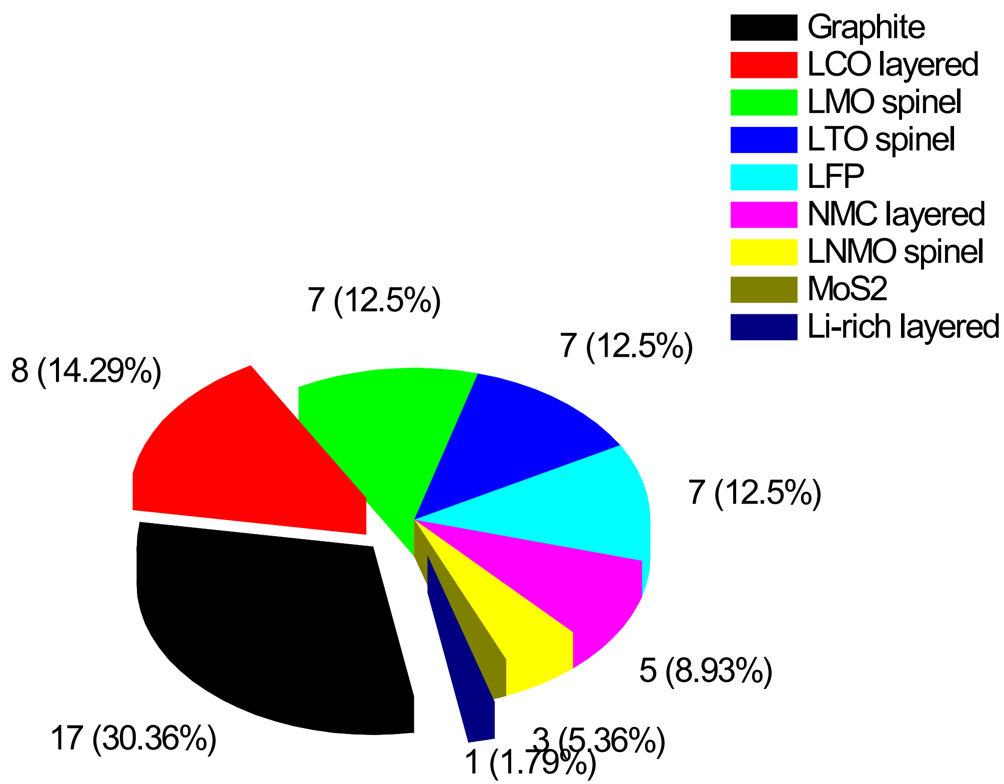
Collaborated with Prof. Liu from NIMTE

B. Qiu and M. Zhang *et. al* submitted, 2016

Accomplishments to Date FY16
Operando Neutron Diffraction on Li-ion Batteries



1. **Limited neutron sources**
2. **Need special battery design**
3. **Complicated data analysis**

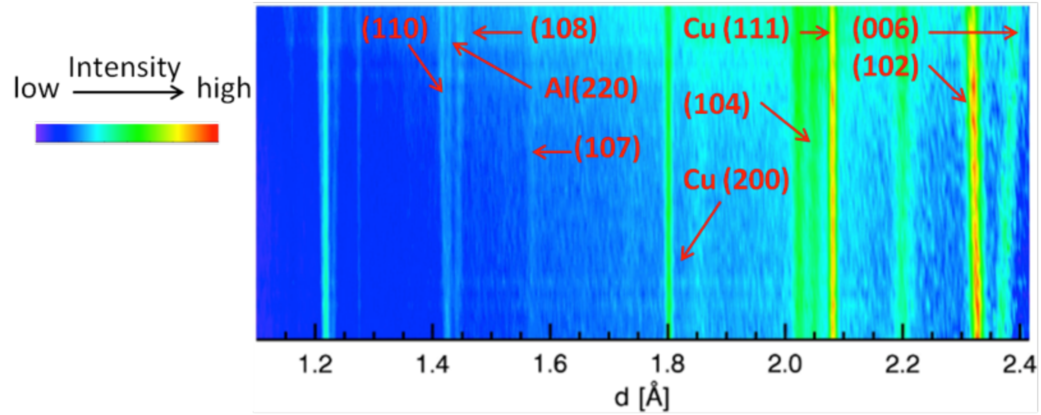


1. **Graphite is common anode, good signals**
2. **Commercialized systems, easy to get**
3. **Cubic systems, easier data analysis**

Technical Achievements
UCSD Third Generation *operando* Neutron

Single layer pouch cell

Only (102) peak from cathode

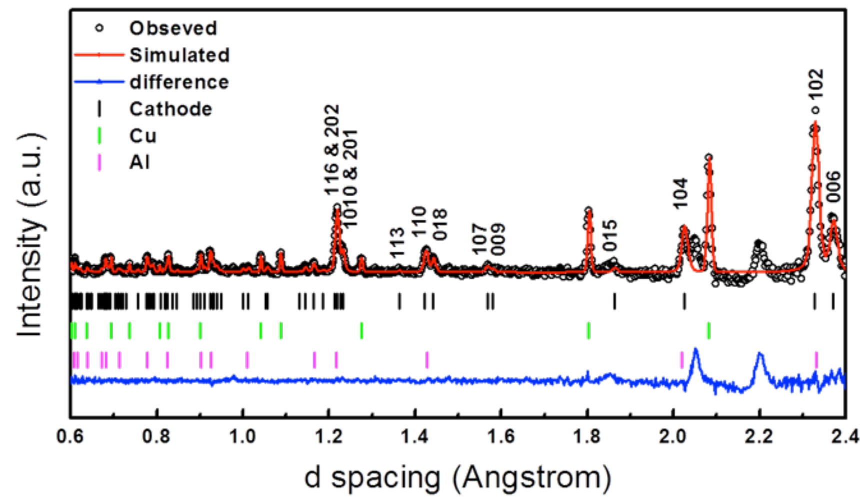


Multi layer pouch cell (C)

Data can be refined, graphite introduce complex phases

Multi layer pouch cell (a-Si and or a-C)

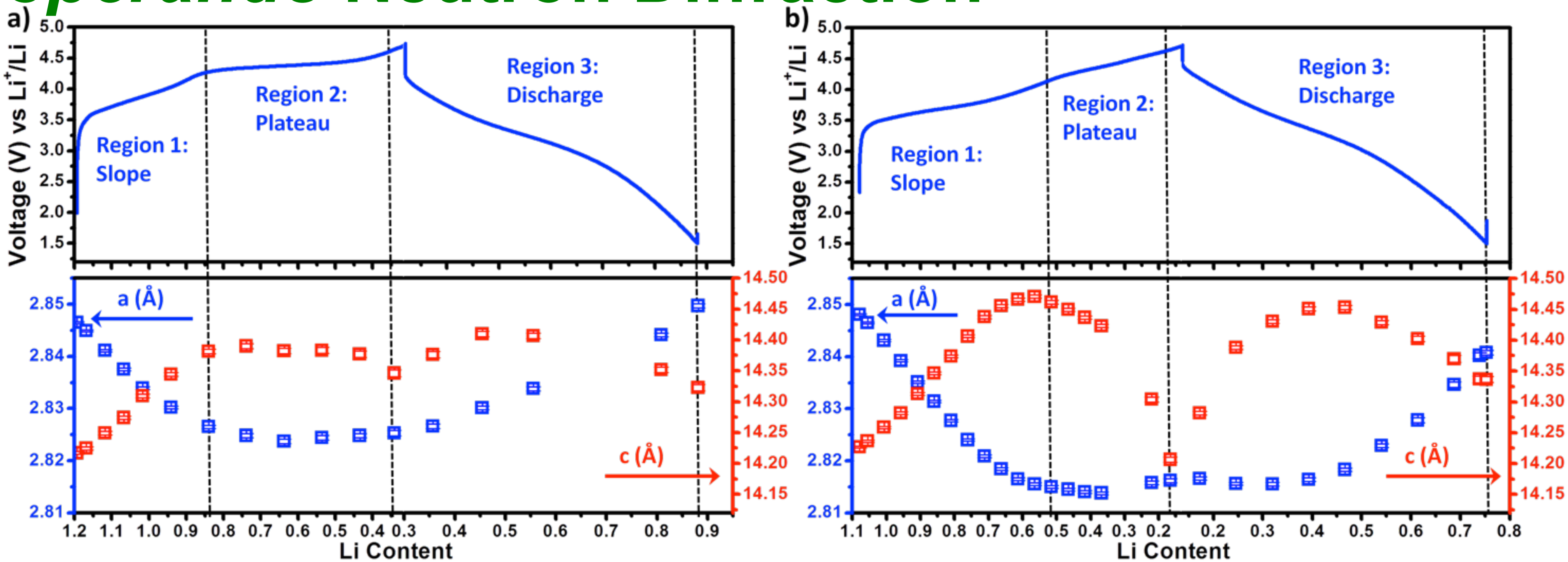
Data can be refined, Improved reliable factor focus on cathode

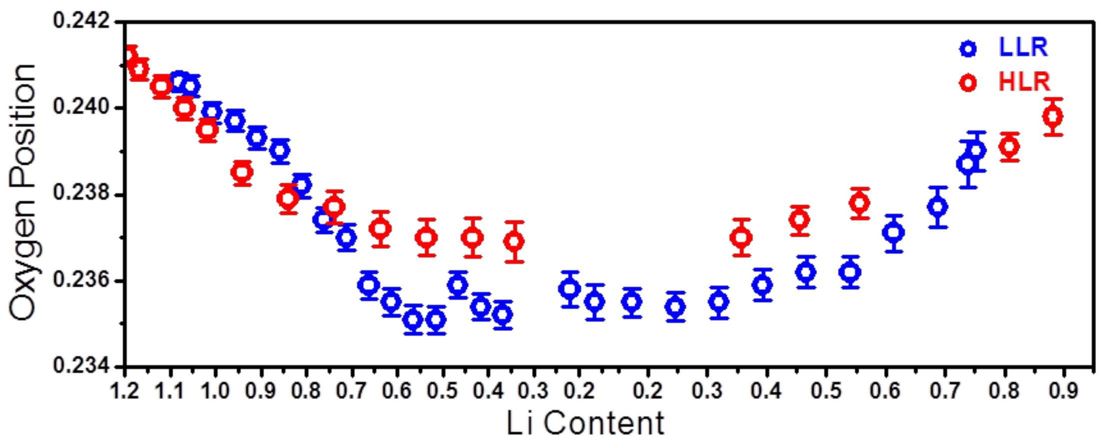


R_{F2} = 9.27% R_{wp} = 1.16% Chi^2 = 1.358

H.D. Liu, Y. Chen, S. Hy, K. An, S. Venkatachalam, D. Qian, M. Zhang, Y.S. Meng, "*Operando* Lithium Dynamics in The Li-Rich Layered Oxide Cathode Material via Neutron Diffraction", Advanced Energy Materials, 2016. 1502143

Technical Achievements
operando Neutron Diffraction





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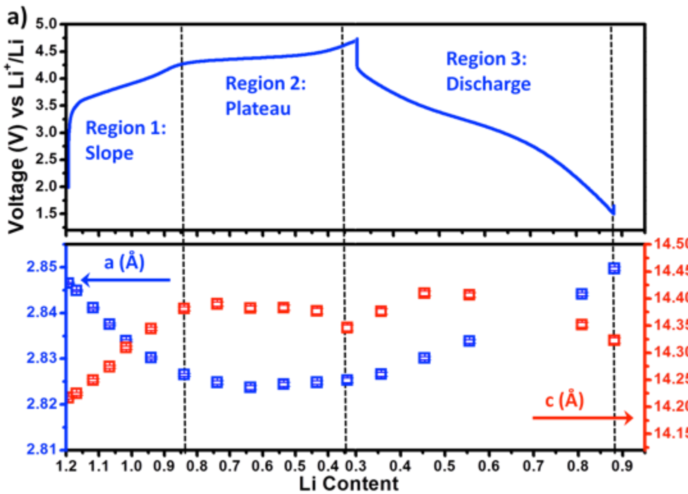
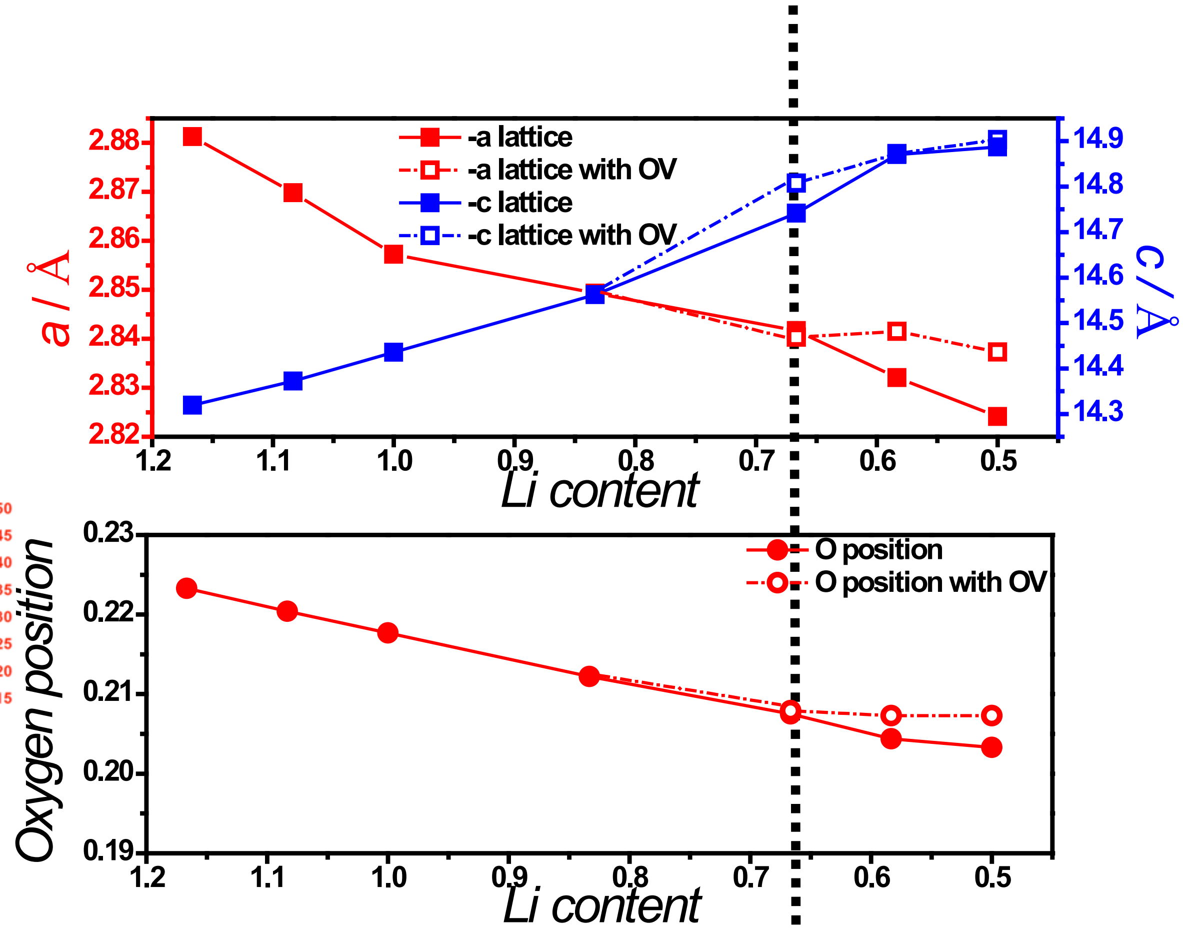
1.-a, -c, oxygen position are well correlated with three regions
2.The -a, -c, oxygen position changes are irreversible

Technical Achievements
Lattice Parameter Changes ND vs. DFT

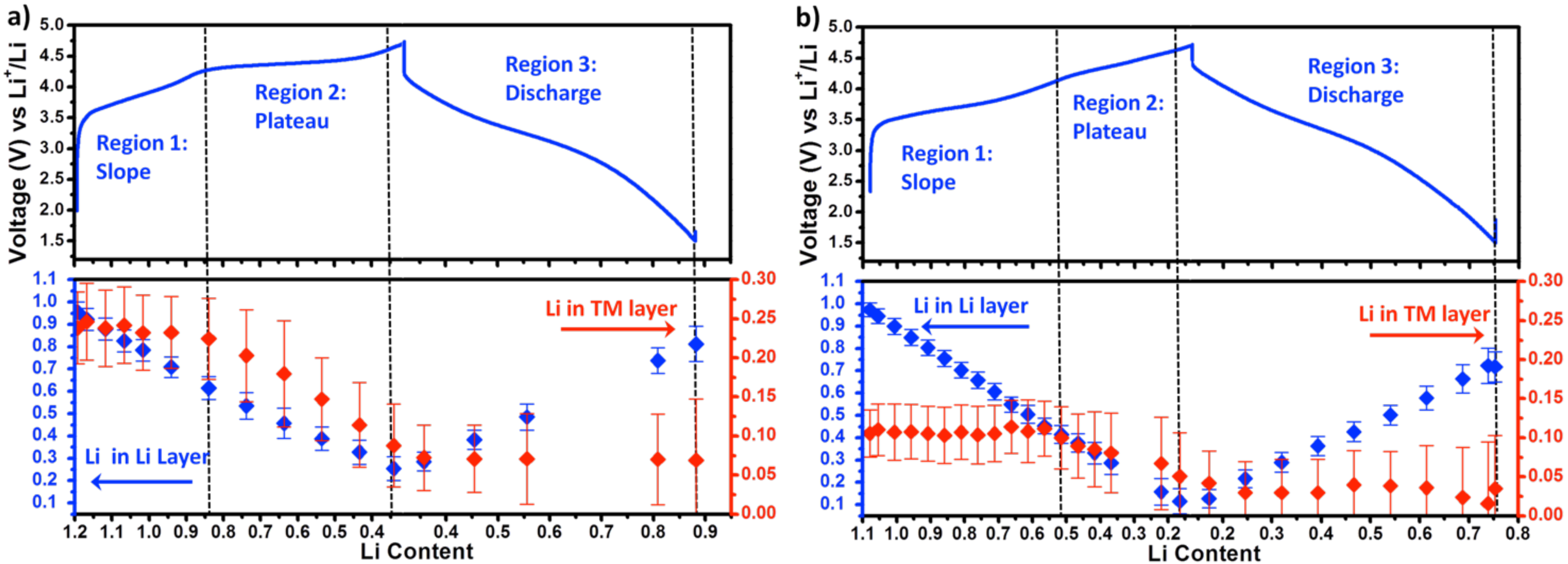


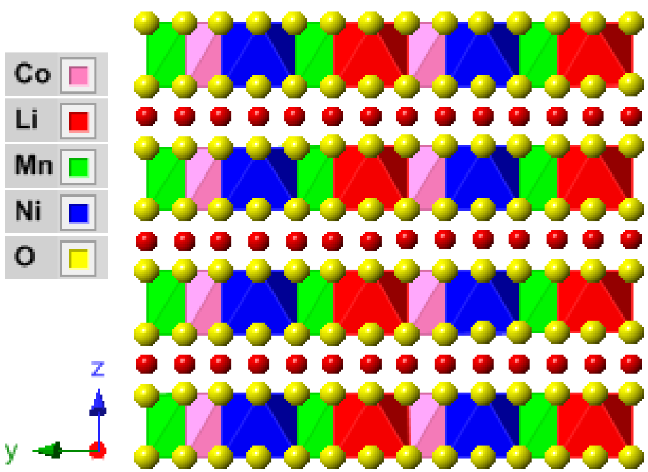


Dilute oxygen vacancy model supports the experimental observations

H.D. Liu, Y. Chen, S. Hy, K. An, S. Venkatachalam, D. Qian, M. Zhang, Y.S. Meng, "*Operando* Lithium Dynamics in The Li-Rich Layered Oxide Cathode Material via Neutron Diffraction", Advanced Energy Materials, 2016, 1502143

Technical Achievements
Lithium De/intercalation Mechanism

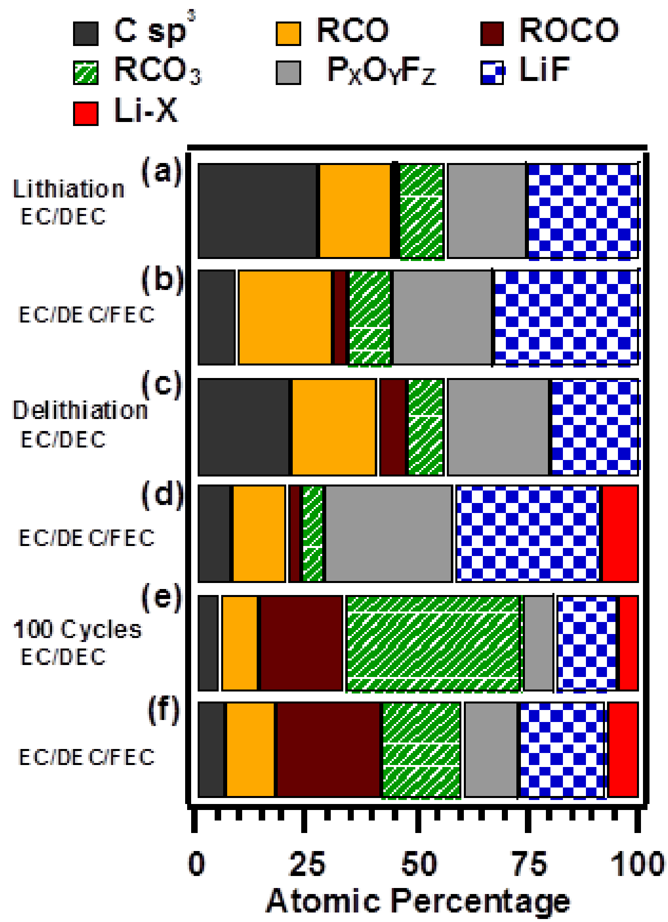


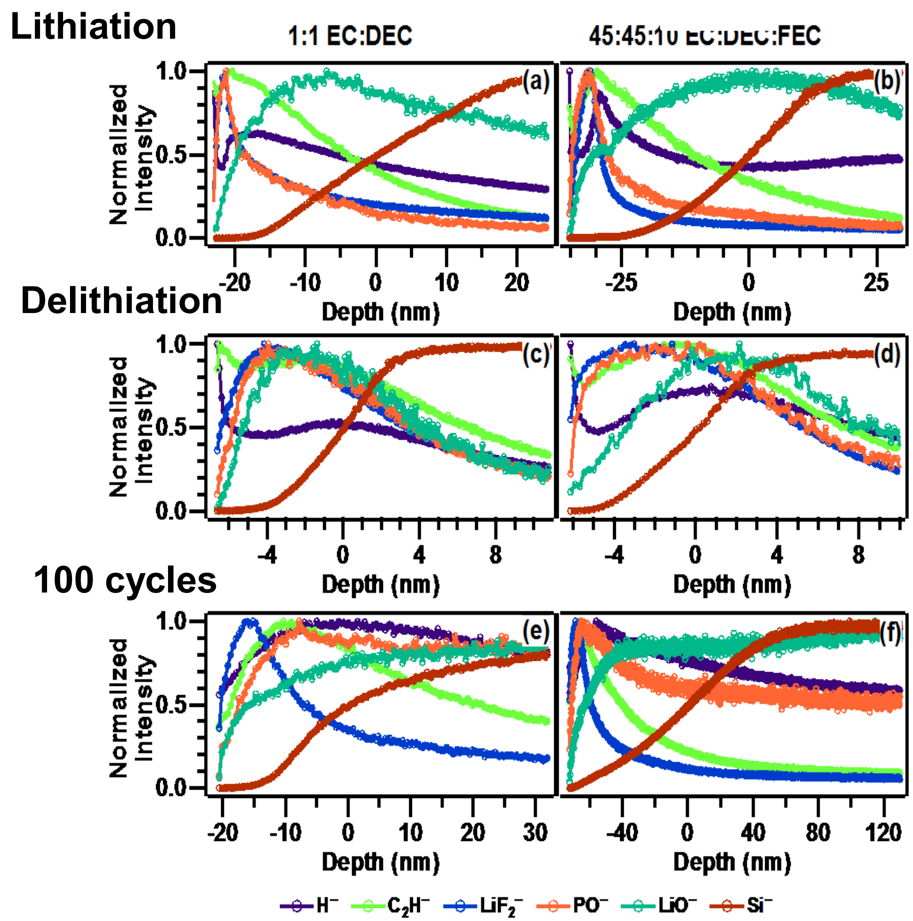


1.Li in Li layer extracted out first
2.Most of Li in TM layer extracted out during plateau region
3.Li inserted back to Li layer during discharge

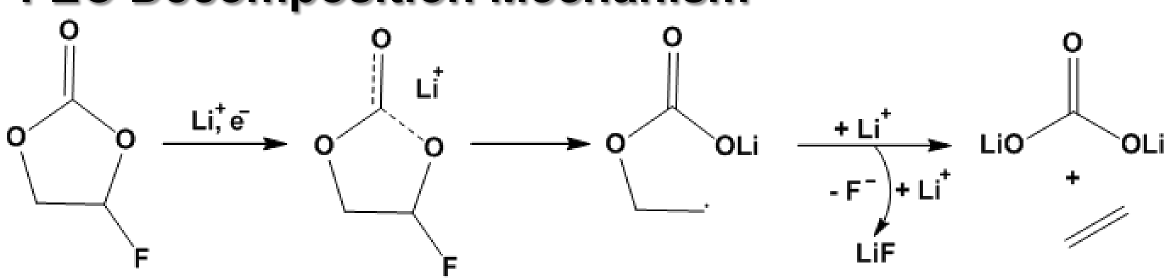
H.D. Liu, Y. Chen, S. Hy, K. An, S. Venkatachalam, D. Qian, M. Zhang, Y.S. Meng, "*Operando* Lithium Dynamics in The Li-Rich Layered Oxide Cathode Material via Neutron Diffraction", **Advanced Energy Materials,** 2016 1502143

Accomplishments to Date FY16
Deciphering the effect of FEC on a-Si thin film





FEC Decomposition Mechanism

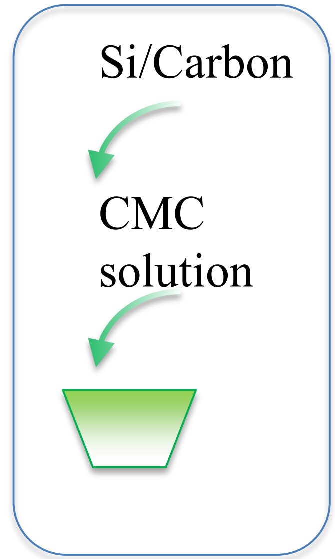


J. Alvarado, K.J. Shroder, T.A Yersak, J. Li, N. Dudney, L. Webb, K.J Stevenson, Y.S Meng **Chem .Mater.**, 2015, 27 (16), 5531

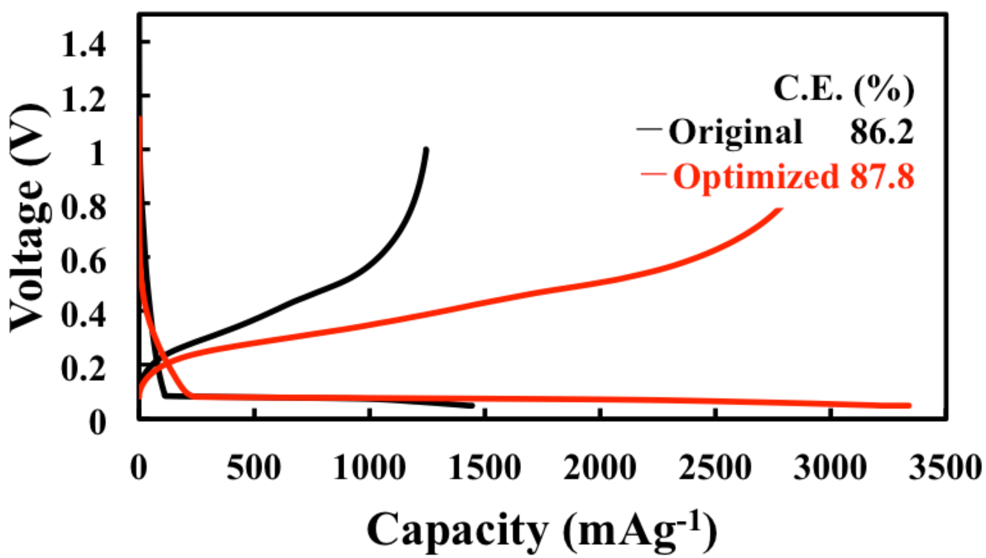
Technical Achievements
Optimization of Si composite electrode

1st step: Mixer
CMC solution

2nd step: Ball Mill
Silicon/Carbon



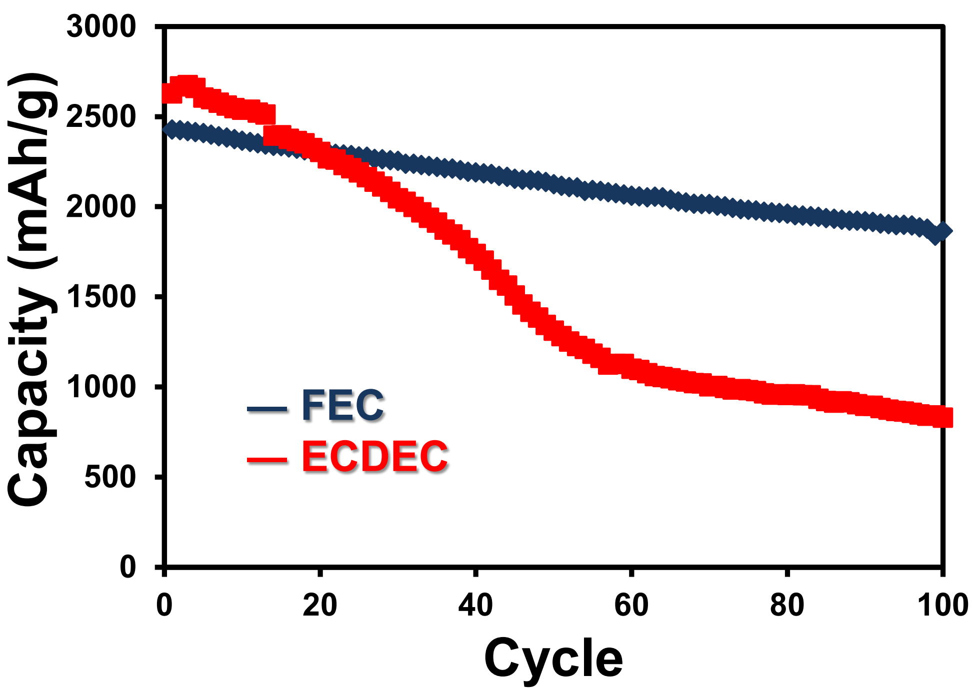
3rd step:
Homogenizer

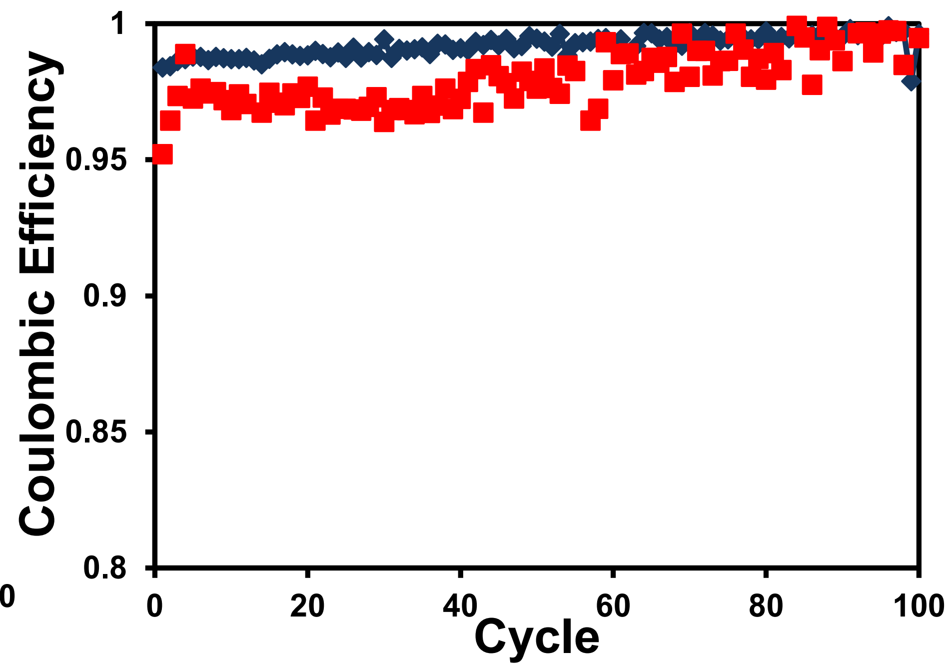


Electrolyte: 1M $LiPF_6$ (1:1) EC/DEC
Voltage Range: 1.0V-0.05V

Vigorously mixing the electrode resulted in less particle agglomeration, this significantly improved the first cycle performance and Coulombic efficiency

Accomplishments to Date FY16
Effect of FEC additive on composite Si electrode



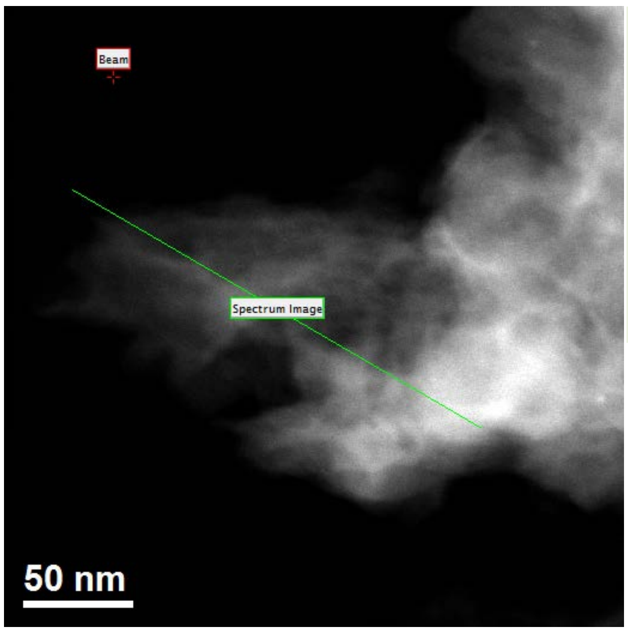


Cycling Parameters:
C rate: C/10
Voltage Range: 1.0V-0.05V

- ❑ FEC additive improves both capacity retention and coulombic efficiency
- ❑ The electrode cycled with FEC only lost 24% capacity

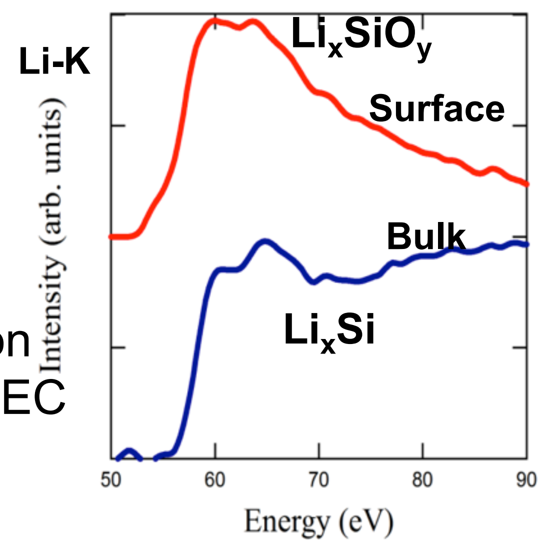
Accomplishments to Date FY16
STEM-EELS Analysis from Cycled Si Nanoparticles

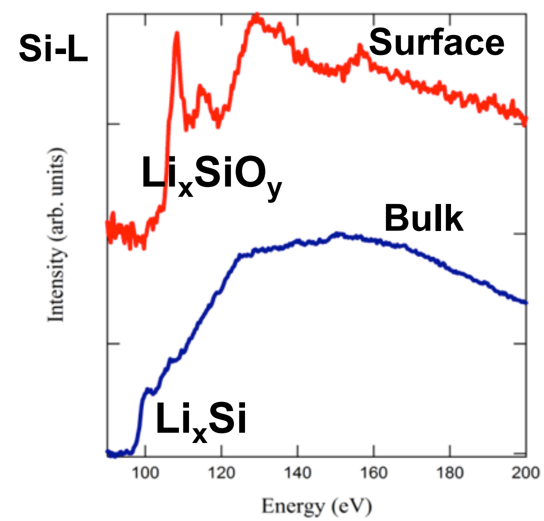
STEM-EELS: is a powerful technique for characterizing Si anode in Li-ion batteries.
Challenge: Lithiated silicon (Li_xSi) alloys and SEI are **extremely beam sensitive**; therefore, STEM/EELS conditions were optimized to minimize beam damage and achieve high spatial resolution.



- ❑ To reduce beam damage:
- ❑ Large area scans were done with a total electron dose of only 620 e/Å^2
- ❑ In order to reduce diffusion processes and also contamination, the samples were also cooled to LN_2 temperature

- ❑ STEM image of first lithiation
- ❑ Electrode cycled with EC:DEC



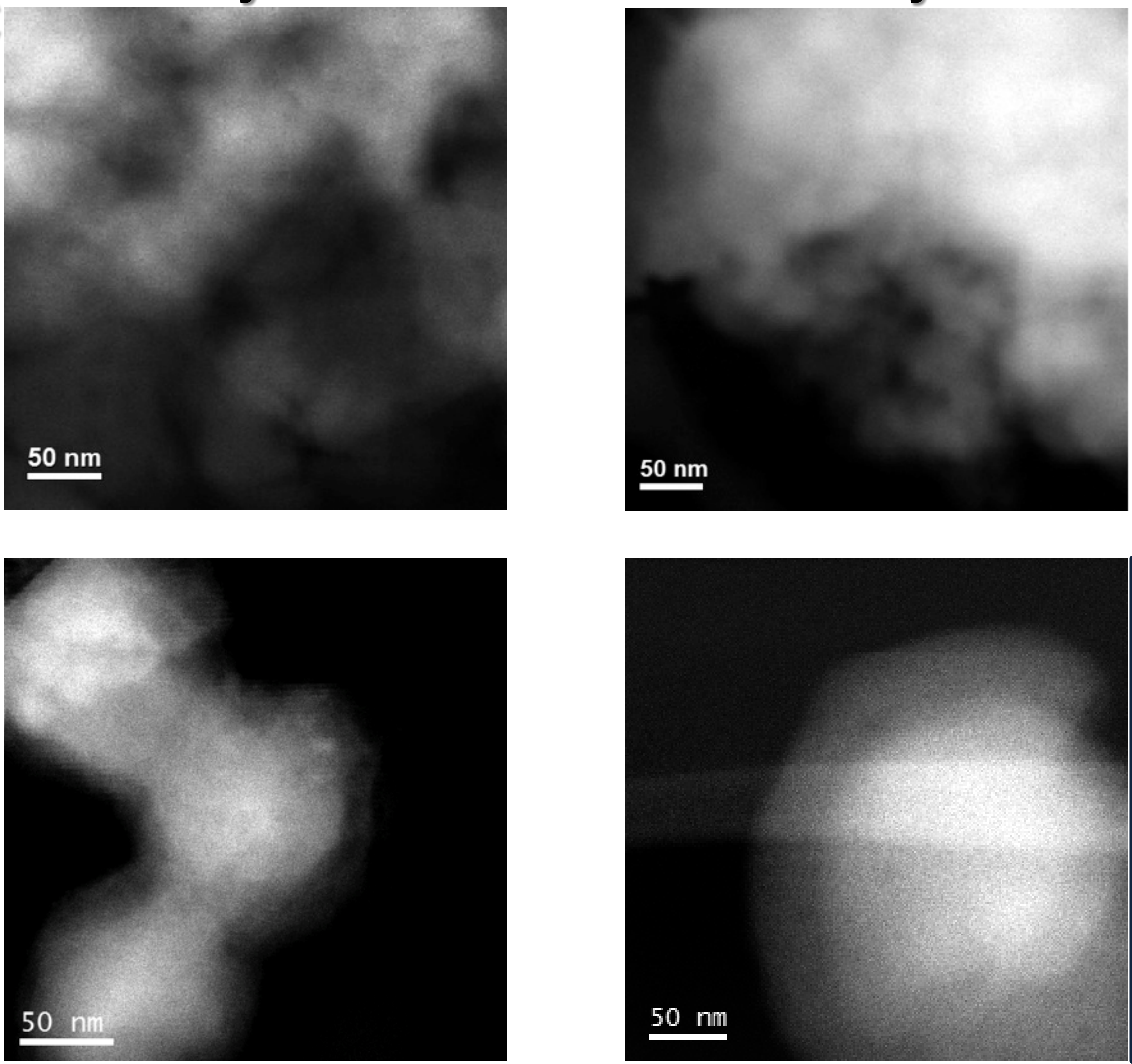


Accomplishments to Date FY16
Direct evidence of SEI morphology

First Cycle **Fifth Cycle**

EC:DEC

FEC



After first cycle particles are immersed in a porous SEI

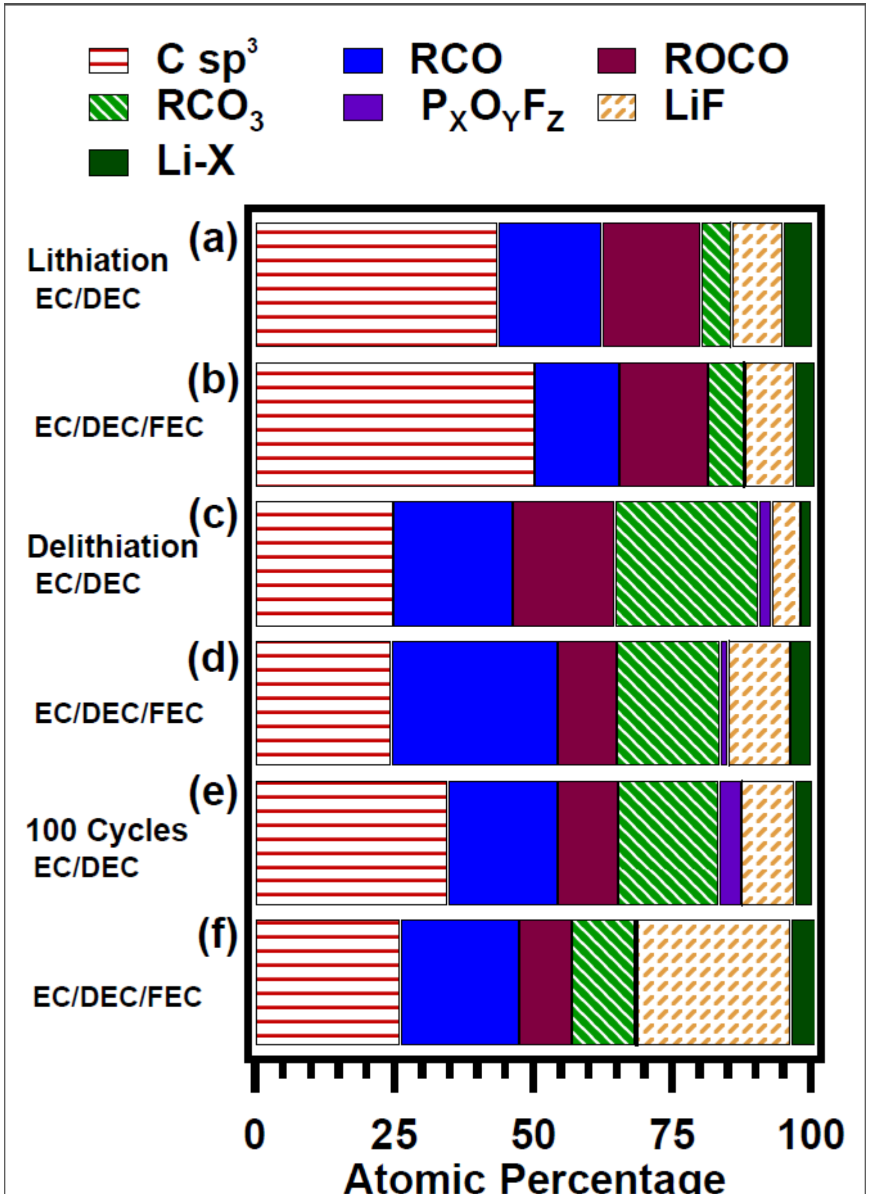
After 5 cycles Si particles are no longer visible due to the SEI

FEC produces a dense thick SEI on the first cycle

Particles maintain uniform shape throughout electrochemical cycling

Sina, M, Alvarado, J, Shobukawa, H, Alexander, C, Stevenson, K, Meng, Y.S, Manuscript in preparation

Accomplishments to Date FY15
XPS analysis on cycled Si composite electrode



Given that STEM EELS is a local technique, XPS was used as a complimentary tool

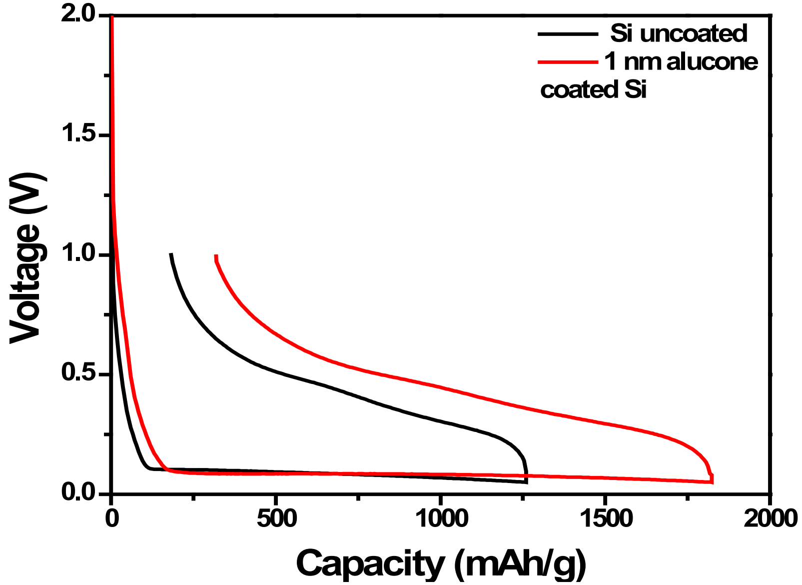
Confirms the EELS results

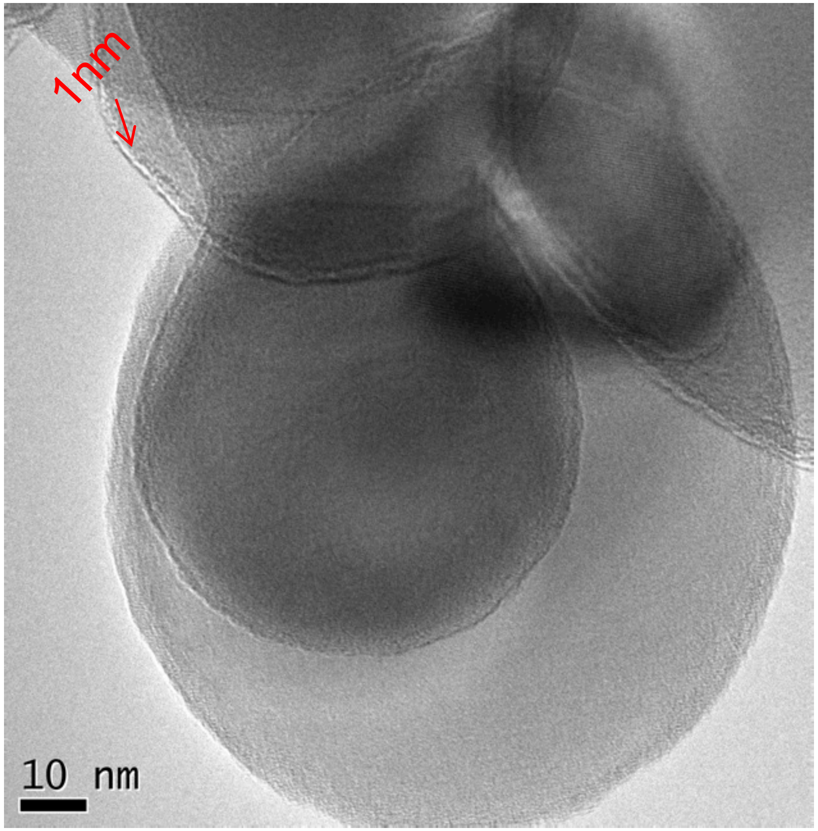
EC:DEC forms more organic products throughout electrochemical cycling

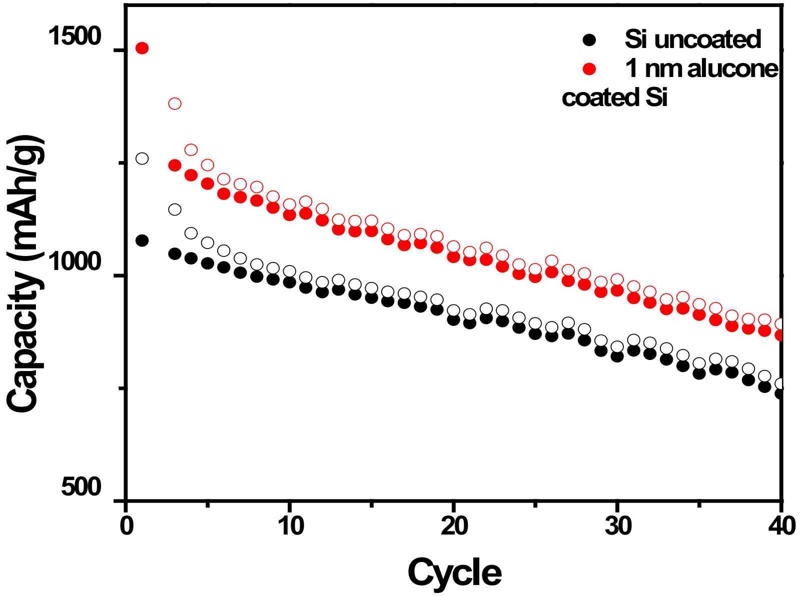
Electrode cycled with **FEC** contains more inorganic compounds, LiF, and less Li_2CO_3

Sina, M, Alvarado, J, Shobukawa, H, Alexander, C, Stevenson, K, Meng, Y.S, Manuscript in preparation

Accomplishments to Date FY16
MLD coating on Si nanoparticles







Cycling Parameters:
C rate: C/10
Voltage Range: 1.0V-0.05V
Electrolyte: EC:DEC

Responses to Previous Year Reviewers' Comments

Comment: the PI has demonstrated a cathode capable of delivering greater than 300 mAh/g with decent cycling stability, where voltage-fading of lithium manganese rich (LMR) was also shown to be mitigated through morphology control rather than surface coating; however, the 80 cycle is still not convincing enough to claim to be effective, although the results are encouraging.
Response: We thank the reviewer for the positive feedback. Lately we have demonstrated cycle life over 250 cycles. Once the paper is accepted for publication, we will show the data to the public.

Comment: PI plans to study the chemical stability of SEI upon cycling, but asked about any plans to study the mechanical property of SEI.
Response: We plan to collaborate with Dr. Yue Qi (MSU) and Dr. Xincheng Xiao (GM) , who are specialized in mechanical properties of SEI

Comment: The reviewer mentioned that the PI should also add modelling components to explain the results.
Response: We have added modeling of Electron Energy Loss Spectroscopy (EELS) to our major research efforts in FY 16.

Collaborations

Dr. Ke An (SNS – Operando ND)

Dr. Nancy Dudney (a-Si thin film)

Dr.Subramanian Venkatachalam (Multilayer Operando Neutron Cell)

Dr. Keith Stevenson and Dr. Anthony Delia (XPS, TOF-SIMS access)

Dr. Chunmei Ban (MLD coatings)

Dr. Zhaoping Liu (Surface Modification)
Dr. Bao Qiu (Surface Modification)

Summary

- Developed a novel gas-solid interfacial modification method for Li-rich cathodes to improve the Li transportation and minimize the voltage decay during cycling

- Identified the path-specific Li dynamics, lattice dynamics, and lattice oxygen evolution in Li-rich layered oxides via *operando* neutron diffraction

- Extended surface characterization techniques consisting of STEM/EELS, XPS, and TOF-SIMS to identifying the SEI compositions and morphology in Si-based anode materials

- By using amorphous silicon thin film model system, we have investigated the effect of FEC co-solvent and other additives in promoting a stable SEI formation

- Direct visualization of SEI morphology using STEM to determine the effect of FEC on composite Si electrodes